## PCT/EP99/03561

## Detergents comprising amylase and color transfer inhibitor

The present invention relates to enzyme containing detergents comprising besides customary constituents an amylase from Bacillus amyloliquefaciens and an active color transfer inhibiting substance.

Laundry detergents, in addition to the ingredients vital to the laundering process, such as surfactants and builder materials, generally comprise further constituents, which may be grouped together under the heading of wash auxiliaries and which embrace such different active substance groups as foam regulators, 15 graving inhibitors, bleaches, bleach activators, and color transfer inhibitors. Such auxiliaries also include substances which assist the surfactant performance by means of enzymatic degradation of stains present on the textile. The same applies, mutatis 20 mutandis, to cleaning products for hard surfaces. As well as the proteases, which assist in removing proteins, and the fat-cleaving lipases, particular importance in this context attaches to the amylases. Amylases have the function of facilitating the removal 2.5 of starchy stains by means of catalytic hydrolysis of the starch polysaccharide, and have been used for this purpose for a fairly long time in dishwashing detergents, but also in detergents for use in textile laundering. In by far the great majority of cases the 30 amylase involved has comprised a heat-stable amylase from Bacillus licheniformis, which is customary in commerce under the designation Termamyl®, for example. More recently, there has been increased use in such compositions of genetically manipulated amylases; that 35 is, amylases whose amino acid sequence has been altered, using gene technology methods, in comparison to naturally occurring amylases. As well as increasing their capacity to perform, the objective of genetically

modifying amylases is essentially to enhance the stability of the enzyme, especially their stability to attack by oxidizing agents. One approach toward achieving this objective, which was proposed in International Patent Application WO 94/18314, consists in removing particularly oxidation-susceptible amino acids, such as methionine, tryptophan, cysteine or tyrosine, from the amino acid sequence of the amylase, or replacing them by other amino acids more stable to 10 oxidation. A similar approach is proposed in International Patent Application WO 95/21247, which recommends replacing at least one methionine in the amylase amino acid sequence by an amino acid which is neither methionine nor cysteine.

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Although such genetic modifications may lead to improved amylase stability under certain application conditions, they do not help to increase the contribution of the amylase to the wash or cleaning performance of corresponding compositions comprising the amylase.

It has surprisingly now been found that the combination of a naturally occurring  $\alpha$ -amylase with color transfer inhibitors leads to unexpectedly synergistic performance improvements when used in detergents.

The invention accordingly provides an amylase containing detergent which comprises  $\alpha$ -amylase from Bacillus amyloliquefaciens and a percarboxylic acid and/or its alkali metal salt, as well as customary incredients compatible with such constituents.

The invention further provides for the use of such a 35 combination for enhancing the cleaning performance of detergents, especially with respect to starchy stains, when used in detergent solutions, especially aqueous detergent solutions. The invention further provides for the use of such a combination for preventing the transfer of textile dyes from dyed textiles to undyed or different-colored textiles when said textiles are laundered together in aqueous solutions, especially aqueous solutions comprising surfactant.

α-Amylase from Bacillus amyloliquefaciens has been known for a long time, for example, from the 10 U.S. Patent US 1 227 374. It is available commercially, for example, under the designation Amylase BAN®.

A composition of the invention contains preferably from 0.001 mg to 0.5 mg, in particular from 0.02 mg to 15 0.3 mg, of amylolytic protein per gram of the overall composition. The protein concentration may be determined using known methods, such as the bicinchonic acid technique (BCA technique, Pierce Chemical Co., Rockford, IL) or the biuret technique (A.G. Gornall, 20 C.S. Bardawill and M.M. David, J. Biol. Chem. 177, 751-766, 1948).

A composition of the invention contains preferably from 0.1% by weight to 2% by weight, in particular 0.2% by 25 weight to 1% by weight, of color transfer inhibitor, which in one preferred embodiment of the invention is a polymer of vinylpyrrolidone, vinylimidazole, vinylpyridine N-oxide, or a copolymer of these. It is possible to use both the polyvinylpyrrolidones, known example from European Patent Application EP 0 262 897, with molar weights of from 15,000 to 50,000, and the polyvinylpyrrolidones known from International Patent Application WO 95/06098, having molar weights of more than 1,000,000, in particular 35 1,500,000 to 4,000,000, the imidazole/N-vinylpyrrolidone copolymers known German Patent Applications DE 28 14 287 or DE 38 03 630 or from International Patent Applications WO 94/10281, WO 94/26796, WO 95/03388 and WO 95/03382, the

polyvinyloxazolidones known from German Patent Application DE 28 14 329, the copolymers based on vinvl monomers and carboxamides that are known from European Patent Application EP 610 846, the polyesters polyamides containing pyrrolidone groups that are known from International Patent Application WO 95/09194, the grafted polyamidoamines and polyethyleneimines known from International Patent Application WO 94/29422, the polymers with amide groups from secondary amines that 10 are known from German Patent Application DE 43 28 254, the polyamine N-oxide polymers known from International Patent Application WO 94/02579 or European Patent Application EP 0 135 217, the polyvinyl alcohols known from European Patent Application EP 0 584 738, and the 15 copolymers based on acrylamidoalkenylsulfonic acids are known from European Patent Application EP 0 584 709. However, it is also possible to use enzymatic systems, comprising a peroxidase and hydrogen peroxide or a substance which in water provides 20 hydrogen peroxide, as are known, for example, from International Patent Applications WO 92/18687 WO 91/05839. The addition of a mediator compound for the peroxidase, for example, an acetosyringone known from International Patent Application WO 96/10079, a 25 phenol derivative known from International Patent Application WO 96/12845, or a phenothiazine phenoxazine known from International Patent Application WO 96/12846, is preferred in this case, it being also possible to use abovementioned active polymeric color transfer inhibitor substances as well. Polyvinylpyrrolidone for use in compositions of the invention preferably has an average molar mass in the range from 10,000 to 60,000, in particular in the range from 25,000 to 50,000. Among the copolymers, preference is given to those of vinylpyrrolidone and vinylimidazole in a molar ratio of 5:1 to 1:1 having an average molar mass in the range from 5000 to 50,000, in particular from 10,000 to 20,000.

In addition to the active substance combination used in accordance with the invention, the detergents of the invention, which may be present as solids, especially pulverulent solids, in postcompacted particle form, as homogeneous solutions or suspensions may in principle comprise all known ingredients which are customary in such compositions. The compositions of the invention particular comprise builder in substances, surfactants, additional bleaches based on organic 10 and/or inorganic peroxygen compounds, bleach activators, water miscible organic solvents, additional enzymes, sequesterants, electrolytes, pH regulators, and further auxiliaries, such as optical brighteners, graying inhibitors, foam regulators, and also dyes and 15 fragrances.

The compositions of the invention may comprise a surfactant or two or more surfactants, suitable surfactants comprising in particular anionic surfactants, nonionic surfactants and mixtures thereof, but also cationic, zwitterionic and amphoteric surfactants

Suitable nonionic surfactants are, in particular, alkyl 2.5 glycosides and ethoxylation and/or propoxylation products of alkyl glycosides or linear or branched alcohols having in each case 12 to 18 carbon atoms in the alkyl moiety and from 3 to 12, preferably from 4 to 10, alkyl ether groups. It is also possible to use corresponding ethoxylation and/or propoxylation products of N-alkylamines, vicinal diols, fatty acid esters and fatty acid amides, which in terms of the alkyl moiety correspond to the aforementioned long chain alcohol derivatives, and also alkylphenols having 35 5 to 12 carbon atoms in the alkyl radical.

Nonionic surfactants used are preferably alkoxylated, advantageously ethoxylated, especially primary, alcohols having preferably 8 to 18 carbon atoms and on

average from 1 to 12 mol of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical may be linear or, preferably, methyl-branched in position 2 and/or may comprise linear and methyl-branched radicals in a mixture, as are commonly present in oxo alcohol radicals. In particular, however, preference is given to alcohol ethoxylates containing linear radicals from alcohols of natural origin having 12 to 18 carbon atoms, e.g., from coconut, palm, tallow fatty or oleyl 10 alcohol and on average from 2 to 8 EO per mole of alcohol. Preferred ethoxylated alcohols include, for example, C12-14 alcohols containing 3 EO or 4 EO, C9-11 alcohols containing 7 EO, C13-15 alcohols containing 3 EO, 5 EO, 7 EO or 8 EO,  $C_{12-18}$  alcohols containing 15 3 EO, 5 EO or 7 EO, and mixtures thereof, such as mixtures of  $C_{12-14}$  alcohol containing 3 EO and  $C_{12-18}$ containing 7 EO. The stated degrees ethoxylation represent statistical mean values, which for a specific product may be an integer or a fraction. 2.0 Preferred alcohol ethoxylates have a narrowed homolog distribution (narrow range ethoxylates, NREs). addition to these nonionic surfactants it is also possible to use fatty alcohols containing more than 12 EO. Examples thereof are (tallow) fatty alcohols 2.5 containing 14 EO, 16 EO, 20 EO, 25 EO, 30 EO or 40 EO. Especially in detergents for use in machine dishwashing processes, it is common to use extremely low-foaming compounds. These include, preferably, C12-C18 alkyl polyethylene glycol-polypropylene glycol ethers having in each case up to 8 mol of ethylene oxide and propylene oxide units in the molecule. However, it is also possible to use other nonionic surfactants which are known to be low-foaming, such as, for example, C12-C18 alkyl polyethylene glycol-polybutylene glycol ethers having in each case up to 8 mol of ethylene oxide and butylene oxide units in the molecule, and also endgroup-capped alkyl polyalkylene glycol mixed ethers. Particular preference is also given to the hydroxyl-containing alkoxylated alcohols as are

described in European Patent Application EP 0 300 305, referred to as hydroxy mixed ethers. The nonionic surfactants also include alkyl glycosides of the general formula RO(G)x, where R is a primary straight-5 chain or methyl-branched aliphatic radical, especially an aliphatic radical methyl-branched in position 2, containing 8 to 22, preferably 12 to 18, carbon atoms, and G represents a glycose unit having 5 or 6 carbon atoms, preferably glucose. The degree of oligomerization, x, which indicates the distribution of monoglycosides and oligoglycosides, is any desired number - which, as a variable to be determined analytically, may also be a fraction - between 1 and 10; preferably, x is from 1.2 to 1.4. Further suitable surfactants are polyhydroxy fatty acid amides of the formula (II)

where R<sup>1</sup>CO is an aliphatic acyl radical having 6 to 22 carbon atoms, R<sup>2</sup> is hydrogen or an alkyl or hydroxyalkyl radical having 1 to 4 carbon atoms, and [Z] is a linear or branched polyhydroxyalkyl radical having 3 to 10 carbon atoms and from 3 to 10 hydroxyl groups. The polyhydroxy fatty acid amides are derived preferably from reducing sugars having 5 or 6 carbon atoms, especially glucose. The group of the polyhydroxy fatty acid amides also includes compounds of the formula (III)

$$R^{4}-O-R^{5}$$
  
|  
35  $R^{3}-CO-N-[Z]$  (III),

where R<sup>3</sup> is a linear or branched alkyl or alkenyl radical having 7 to 12 carbon atoms, R<sup>4</sup> is a linear, branched or cyclic alkylene radical or an arylene radical having 2 to 8 carbon atoms and R<sup>5</sup> is a linear,

branched or cyclic alkyl radical or an aryl radical or an oxyalkyl radical having 1 to 8 carbon atoms. preference being given to C1-C4 alkyl radicals or phenyl radicals, and [Z] is a linear polyhydroxyalkyl radical whose alkyl chain is substituted by at least two hydroxyl groups, or alkoxylated, preferably ethoxylated or propoxylated, derivatives of said radical. Here too, [Z] is preferably obtained by reductive amination of a sugar such as glucose, fructose, maltose, lactose, 10 galactose, mannose, or xvlose. The N-alkoxv- or N-arvloxy-substituted compounds may then be converted to the desired polyhydroxy fatty acid amides, accordance with the example, in teaching of International Patent Application WO 95/07331 bv 15 reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst. A further class of nonionic surfactants used with preference, which are used either as sole nonionic surfactant or in combination with other nonionic surfactants, in particular together with alkoxylated fatty alcohols and/or alkyl glycosides, are 20 alkoxylated, preferably ethoxylated, or ethoxylated and propoxylated, fatty acid alkyl esters, preferably having 1 to 4 carbon atoms in the alkyl chain, especially fatty acid methyl esters, as are described, 2.5 for example, in Japanese Patent Application JP 58/217598, or those prepared preferably by the process described in International Patent Application WO 90/13533. Nonionic surfactants of the amine oxide type, examples being N-cocoalkyl-N,N-dimethylamine oxide and N-tallowalkyl-N,N-dihydroxyethylamine oxide, and of the fatty acid alkanolamide type, may also be suitable. The amount of these nonionic surfactants is preferably not more than that of the ethoxylated fatty alcohols, in particular not more than half thereof. 35 Further suitable surfactants include those known as gemini surfactants. This term is used generally to refer to those compounds which possess two hydrophilic groups per molecule. These groups are generally separated from one another as a result of what is known

as a spacer. This spacer is generally a carbon chain, which should be long enough to give the hydrophilic groups a sufficient spacing to allow them to act independently of one another. Surfactants of this kind are generally notable for an unusually low critical micelle concentration and the ability to reduce greatly the surface tension of water. In exceptional cases, however, the expression gemini surfactants is used to embrace not only dimeric but also, correspondingly, 10 trimeric surfactants. Examples of suitable gemini surfactants are sulfated hydroxy mixed ethers in accordance with German Patent Application DE 43 21 022 or dimer alcohol bis- and trimer alcohol tris-sulfates and ether sulfates in accordance with German Patent 15 Application DE 195 03 061. Endgroup-capped dimeric and trimeric mixed ethers in accordance with German Patent Application DE-A-195 13 391 are notable in particular for their bi- and multifunctionality. Thus endgroup-capped surfactants possess good wetting 20 properties and are low-foaming, so making them particularly suitable for use in machine washing or cleaning processes. However, it is also possible to use gemini-polyhydroxy fatty acid amides or polypolyhydroxy fatty acid amides, as described in International Patent Applications WO 95/19953, WO 95/19954, and WO 95/19955. 2.5

Suitable anionic surfactants are, in particular, soaps and those containing sulfate or sulfonate groups. Preferred surfactants of the sulfonate type Co-12 alkylbenzenesulfonates, olefinsulfonates, of alkenesulfonates and hvdroxvalkanesulfonates, and also disulfonates, as are obtained, for example, from C12-18 monoolefins having a terminal or internal double bond by sulfonating with gaseous sulfur 35 trioxide followed by alkaline or acidic hydrolysis of sulfonation products. Also alkanesulfonates, which are obtained from C12-18 alkanes, for example, by sulfochlorination or sulfoxidation with subsequent hydrolysis or neutralization, respectively.

Likewise suitable, in addition, are the esters of α-sulfo fatty acids (ester sulfonates), e.g., the α-sulfonated methyl esters of hydrogenated coconut, palm kernel or tallow fatty acids, which are prepared by α-sulfonation of the methyl esters of fatty acids of plant and/or animal origin having 8 to 20 carbon atoms in the fatty acid molecule, followed by neutralization to give water-soluble mono-salts. Preferably, these comprise the a-sulfonated esters of hydrogenated coconut, palm, palm kernel or tallow fatty acids, it 10 being possible as well for sulfonation products of unsaturated fatty acids, e.g. oleic acid, to be present in small amounts, preferably in amounts of not more than about 2 to 3% by weight. Particular preference is 15 given to  $\alpha$ -sulfo fatty acid alkyl esters having an alkyl chain of not more than 4 carbon atoms in the ester group, examples being methyl esters, ethyl propvl esters, and butvl esters. particular advantage, the methyl esters of the  $\alpha$ -sulfo 20 fatty acids (MES) are used, and also their saponified di-salts. Further suitable anionic surfactants are sulfated fatty acid glycerol esters which are the monoesters, diesters and triesters, and mixtures thereof, obtained in the preparation 2.5 esterification of a monoglycerol with from 1 to 3 mol of fatty acid or in the transesterification of trialycerides with from 0.3 to 2 mol of alycerol. Preferred alk(en)vl sulfates are the alkali metal salts, and especially the sodium salts, of the sulfuric monoesters of C12-C18 fatty alcohols, examples being those of coconut fatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or of C10-C20 oxo alcohols, and those monoesters of secondary alcohols of this chain length. Preference is also given 35 to alk(en)yl sulfates of said chain length which contain a synthetic straight-chain alkyl radical prepared on a petrochemical basis, these sulfates possessing degradation properties similar to those of the corresponding compounds based on fatty-chemical raw

materials. From a detergents standpoint, C12-C16 alkyl sulfates and C12-C15 alkyl sulfates, and also C14-C15 alkyl sulfates, are particularly preferred. addition, 2,3-alkyl sulfates, which may for example be prepared in accordance with US Patents 3,234,258 or 5,075,041 and obtained as commercial products from Shell Oil Company under the name DAN®, are suitable anionic surfactants. Also suitable are the sulfuric monoesters of the straight-chain or branched C7-21 10 alcohols ethoxylated with from 1 to 6 mol of ethylene oxide, such as 2-methvl-branched C9-11 alcohols containing on average 3.5 mol of ethylene oxide (EO) or  $C_{12-18}$  fatty alcohols containing from 1 to 4 EO. Preferred anionic surfactants further include the salts 15 of alkylsulfosuccinic acid, which are also referred to as sulfosuccinates or as sulfosuccinic esters and which constitute the monoesters and/or diesters sulfosuccinic acid with alcohols, preferably fatty alcohols and especially ethoxylated fatty alcohols. 20 Preferred sulfosuccinates comprise C8-18 fatty alcohol radicals or mixtures thereof. Especially preferred sulfosuccinates contain a fatty alcohol radical derived from ethoxylated fatty alcohols which themselves represent nonionic surfactants. Particular preference 2.5 is given in turn to sulfosuccinates whose fatty alcohol radicals are derived from ethoxylated fatty alcohols having a narrowed homolog distribution. Similarly, it also possible to use alk(en)vlsuccinic acid containing preferably 8 to 18 carbon atoms in the alk(en)vl chain, or salts thereof. Further suitable anionic surfactants include fatty acid derivatives of amino acids, for example, of N-methyltaurine (taurides) and/or of N-methylglycine (sarcosides). Particular preference is given here to sarcosides and to the sarcosinates and, of these, especially the sarcosinates higher fatty acids, which may be mono- or polyunsaturated, such as oleyl sarcosinate. Further suitable anionic surfactants are, in particular, soaps. Suitable soaps include in particular saturated fatty acid soaps, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid, and, in particular, mixtures of soaps derived from natural fatty acids, e.g., coconut, palm kernel, or tallow fatty acids. Together with these soaps, or as substitutes for soaps, it is also possible to use the known alkenylsuccinic salts.

The anionic surfactants, including the soaps, may be present in the form of their sodium, potassium or ammonium salts and also as soluble salts of organic bases, such as mono-, di- or triethanolamine. Preferably, the anionic surfactants are in the form of their sodium or potassium salts, in particular in the form of the sodium salts.

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In laundry detergents of the invention, surfactants are present in proportions of preferably from 5% by weight to 50% by weight, in particular from 8% by weight to 30% by weight, whereas compositions for cleaning hard surfaces, especially for the machine cleaning of kitchen- and tableware, have lower surfactant contents of up to 10% by weight, in particular up to 5% by weight, and preferably in the range from 0.5% by weight to 3% by weight.

A composition of the invention comprises preferably at least one water soluble and/or water insoluble, organic and/or inorganic builder. The water soluble organic builder substances include polycarboxylic acids, especially citric acid and sugar acids, monomeric and polymeric amino polycarboxylic acids, in particular methylglycinediacetic acid, nitrilotriacetic acid and ethylenediaminetetraacetic acid, and also polyaspartic acid, polyphosphonic acids, especially aminotris-(methylenephosphonic acid), ethylenediaminetetrakis-(methylenephosphonic acid) and l-hydroxyethane-1,l-diphosphonic acid, polymeric hydroxy compounds such as dextrin, and also polymeric (poly) carboxylic acids,

especially the polycarboxylates of European Patent EP 0 625 992 or of International Patent Application WO 92/18542 or of European Patent EP 0 232 202, which obtainable by oxidizing polysaccharides respectively, dextrins; polymeric acrylic methacrylic acids, maleic acids and copolymers thereof, which may also contain in copolymerized form small fractions polymerizable substances of carboxylic acid functionality. The relative molecular 10 mass of the homopolymers of unsaturated carboxyclic acids is generally between 3000 and 200,000, that of the copolymers between 2000 and 200,000, preferably from 30,000 to 120,000, based in each case on free acid. A particularly preferred acrylic acid-maleic acid 15 copolymer has a relative molecular mass of from 30,000 to 100,000. Commercially customary products are, for example, Sokalan® CP 5, CP 10 and PA 30 from BASF. Suitable though less preferred compounds of this class are copolymers of acrylic acid or methacrylic acid with vinyl ethers, such as vinyl methyl ethers, vinyl 20 esters, ethylene, propylene and styrene, in which the acid fraction is at least 50% by weight. As water soluble organic builder substances it is also possible terpolymers containing as monomers unsaturated acids and/or their salts and, as the third 2.5 monomer, vinyl alcohol and/or an esterified vinyl alcohol or a carbohydrate. The first acidic monomer or salt thereof is derived from a monoethylenically unsaturated C3-C8 carboxylic acid and, preferably, from 30 C3-C4 monocarboxvlic acid, especially (meth)acrylic acid. The second acidic monomer or salt thereof may be a derivative of a C4-C8 dicarboxylic acid, maleic acid being particularly preferred, and/or a derivative of an allylsulfonic acid substituted in position 2 by an alkyl or aryl radical. Such polymers may be prepared in particular by processes which are described in German Patent DE 42 21 381 and German Patent Application DE 43 00 772, and generally have a relative molecular mass of between 1000 and 200,000.

Further preferred copolymers are those described in German Patent Applications DE 43 03 320 and containing DE 44 17 734, as monomers preferably acrolein and acrylic acid/acrylic acid salts, and/or vinvl acetate. The organic builder especially for the preparation of liquid compositions, may be used in the form of aqueous solutions, preferably aqueous solutions with a strength of from 30 to 50 percent by weight. All said acids are generally used in the form of their water soluble salts, 10 especially their alkali metal salts.

Organic builder substances of this kind may be present, if desired, in amounts of up to 40% by weight, in 15 particular up to 25% by weight, and preferably from 1% by weight to 8% by weight. Amounts close to the stated upper limit are used preferably in pastelike or liquid compositions of the invention, especially those containing water.

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Suitable water soluble inorganic builder materials include, in particular, alkali metal silicates, alkali metal carbonates and alkali metal phosphates, which may be present in the form of their alkaline, neutral or 2.5 acidic sodium or potassium salts. Examples thereof are trisodium phosphate, tetrasodium diphosphate, disodium dihydrogen diphosphate, pentasodium triphosphate, so-called sodium hexametaphosphate. oligomeric trisodium phosphate having degrees of oligomerization from 5 to 1000, especially from 5 to 50, and also the corresponding potassium salts and/or mixtures of sodium and potassium salts. Water insoluble, water dispersible inorganic builder materials used are, in particular, crystalline or amorphous alkali metal alumosilicates, in amounts of up to 50% by weight, preferably not more than 40% by weight, and in liquid compositions in particular from 1% by weight to 5% by weight. Among these, preference is given to the crystalline sodium alumosilicates of detergent quality, especially zeolite A, P and, if appropriate, X, alone or in mixtures, in the form for example of a cocrystallizate of zeolites A and X (Vegobond® AX, a commercial product from Condea Augusta S.p.A.). Amounts close to the stated upper 5 limit are used preferably in solid, particulate compositions. Suitable alumosilicates possess in particular no particles having a size of more than 30 μm, and preferably consist at least 80% by weight of particles having a size below 10 μm. Their calcium binding capacity, which may be determined in accordance with the information in German Patent DE 24 12 837, is generally in the range from 100 to 200 mg of CaO per gram.

15 Suitable substitutes or partial substitutes for said alumosilicate are crystalline alkali metal silicates, which may be present alone or in a mixture with amorphous silicates. The alkali metal silicates which can be used as builders in the compositions of the invention preferably have a molar ratio of alkali metal 20 oxide to SiO2 of below 0.95, in particular from 1:1.1 to 1:12, and may be present in amorphous or crystalline form. Preferred alkali metal silicates are the sodium siliates, especially the amorphous sodium silicates, 2.5 having a molar ratio Na<sub>2</sub>O:SiO<sub>2</sub> of from 1:2 to 1:2.8. Those with a molar ratio Na<sub>2</sub>O:SiO<sub>2</sub> of from 1:1.9 to 1:2.8 may be prepared by the process of European Patent Application EP 0 425 427. As crystalline silicates which may be present alone or in a mixture with amorphous silicates it is preferred to use crystalline phyllosilicates of the general formula NaoSivOov+1.vHoO, where x, the so-called modulus, is a number from 1.9 to 22, in particular from 1.9 to 4, and y is a number from 0 to 33, and preferred values for x are 2, 3 or 4. Crystalline phyllosilicates which fall under this general formula are described, for example, in European Patent Application EP 0 164 514. Preferred crystalline phyllosilicates are those where x in the stated general formula adopts the values 2 or 3. In particular, both

Band δ-sodium disilicates (Na2Si2O5.yH2O) preferred, with  $\beta$ -sodium disilicate, for example, being obtainable by the process described in International Patent Application WO 91/08171.  $\delta$ -Sodium silicates having a modulus of between 1.9 and 3.2 may be prepared accordance with Japanese Patent Applications JP 04/238 809 and JP 04/260 610. In addition, virtually anhydrous crystalline alkali metal silicates of the abovementioned general formula wherein x is a number 10 from 1.9 to 2.1, prepared from amorphous alkali metal silicates, and preparable as described in European Patent Applications EP 0 548 599, EP 0 502 325 EP 0 452 428, may be used in compositions of the invention. In a further preferred embodiment of 15 compositions of the invention, a crystalline sodium phyllosilicate having a modulus of from 2 to 3 is used, as may be prepared from sand and soda by the process of European Patent Application EP 0 436 835. Crystalline sodium silicates having a modulus in the range from 1.9 20 to 3.5, as are obtainable by the processes of European Patents EP 0 164 552 and/or EP 0 294 753, are used in a further preferred embodiment of compositions of the invention. Crystalline sheetlike silicates of abovementioned formula are sold by Clariant GmbH under 2.5 the trade name Na-SKS, e.g., Na-SKS-1 (NaoSiooO45 xHoO, kenyaite), Na-SKS-2 (Na<sub>2</sub>Si<sub>14</sub>O<sub>29</sub>·xH<sub>2</sub>O, magadiite), Na-SKS-3 (Na<sub>2</sub>Si<sub>8</sub>O<sub>17</sub>·xH<sub>2</sub>O) or Na-SKS-4 (Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub>·xH<sub>2</sub>O, makatite). Of these, those particularly suitable include Na-SKS-5 (α-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>), Na-SKS-7 (β-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, natrosilite), Na-SKS-9 (NaHSi>Os·3H>O), Na-SKS-10 (NaHSi>Os·3H>O, kanemite), Na-SKS-11 (t-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>) and Na-SKS-13 (NaHSi<sub>2</sub>O<sub>5</sub>), but especially Na-SKS-6  $(\delta-Na_2Si_2O_5)$ . A review of crystalline phyllosilicates is given, for example, by the articles published in "Hoechst High Chem Magazin 35 14/1993" on pages 33-38 and in "Seifen-Öle-Fette-Wachse, Vol. 116, No. 20/1990" on pages 805-808. In one preferred embodiment of compositions of the invention, use is made of a granular compound of crystalline phyllosilicate and citrate, of crystalline phyllosilicate and abovementioned (co)polymeric polycarboxylic acid, as is described, for example, in German Patent Application DE 198 19 187, or of alkali metal silicate and alkali metal carbonate, as is described, for example, in International Patent Application WO 95/22592 or as is available commercially, for example, under the name Nabion® 15.

Builder substances may be present in the compositions of the invention, if desired, in amounts of up to 90% by weight. They are preferably present in amounts of up to 75% by weight. Laundry detergents of the invention have builder contents of in particular from 5% by weight to 50% by weight.

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Peroxygen compounds suitable for use in compositions of the invention include, in particular, organic peracids peracidic salts of organic acids, phthalimidopercaproic acid, perbenzoic acid or salts of 20 diperdodecanedioic acid, hydrogen peroxide, inorganic salts which give off hydrogen peroxide under washing conditions. including perborate, percarbonate, persilicate and/or persulfate such as Caroate. Where solid peroxygen compounds are to be 2.5 used, they may be employed in the form of powders or granules, which may also have been coated in a manner which is known in principle. Where a composition of the invention does comprise peroxygen compounds, they are present in amounts of preferably up to 50% by weight, in particular from 5% by weight to 30% by weight. The addition of small amounts of known bleach stabilizers such as, for example, of phosphonates, borates and/or metaborates and metasilicates, and also magnesium salts such as magnesium sulfate, may be judicious.

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Bleach activators which may be used are compounds which under perhydrolysis conditions give rise to aliphatic peroxo carboxylic acids having preferably 1 to 10 carbon atoms, in particular 2 to 4 carbon atoms, and/or

substituted or unsubstituted perbenzoic acid. Suitable substances are those which carry O-acyl and/or N-acyl groups of the stated number of carbon atoms, and/or substituted or unsubstituted benzovl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetylethylenediamine (TAED), acylated triazine especially 1,5-diacetyl-2,4-dioxohexaderivatives, hydro-1,3,5-triazine (DADHT), acylated glycolurils, especially tetraacetylglycoluril (TAGU), N-acyl imides, 10 especially N-nonanovlsuccinimide (NOSI), phenolsulfonates, especially n-nonanovlisononanovloxybenzenesulfonate (nor iso-NOBS), carboxylic anhydrides, especially phthalic anhydride, acylated polyhydric alcohols, especially triacetin, 15 ethvlene glycol diacetate, 2,5-diacetoxy-2,5dihydrofuran, and the enol esters known from German Patent Applications DE 196 16 693 and DE 196 16 767, and also acetylated sorbitol and mannitol and/or the mixtures thereof (SORMAN) described in European Patent 20 Application EP 0 525 239, acylated sugar derivatives, especially pentaacetylglucose (PAG), pentaacetvlfructose, tetraacetylxylose and octaacetyllactose, and acetvlated, optionally N-alkylated glucamine gluconolactone, and/or N-acvlated lactams, for example, known 25 N-benzovlcaprolactam, which are from International Patent Applications WO 94/27970. WO 94/28102, WO 94/28103, WO 95/00626, WO 95/14759 and WO 95/17498. The hydrophilically substituted acvlacetals known from German Patent Application DE 196 16 769 and acvllactams described in German Patent Application DE 196 16 770 and in International Patent Application WO 95/14075 are likewise used with preference. The combinations of conventional bleach activators known from German Patent Application 35 DE 44 43 177, may also be used. Such bleach activators, in particular when the abovementioned hydrogen peroxide providing bleaches are present, may be present in customary quantities, preferably in amounts of from 0.5% by weight to 10% by weight, and in particular from 1% by weight to 8% by weight, based on overall composition, but are preferably all absent when the percarboxylic acid essential to the invention is used as the sole bleach.

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In addition to the conventional bleach activators, or instead of them, it is also possible for the sulfonimines known from European Patents EP 0 446 982 and EP 0 453 003 and/or for bleach boosting transition metal salts or transition metal complexes to be present as so-called bleaching catalysts.

Enzymes which may be used in the compositions in addition to the amylase that is essential to the 15 invention include those from the class of the proteases, lipases, cutinases, pullulanases, hemicellulases, cellulases, oxidases, laccases peroxidases, and mixtures thereof. If desired, amylases other than the amylase essential to the invention may be present in addition to it. Particularly suitable 20 active enzymatic substances are those obtained from fungi or bacteria, such as Bacillus subtilis, Bacillus licheniformis, Bacillus lentus, Streptomyces griseus, Humicola lanuginosa, Humicola insolens, Pseudomonas 2.5 pseudoalcaligenes, Pseudomonas cepacia or Coprinus cinereus. The amylase essential to the invention and the enzymes that may be used in addition may - as described, for example, in European Patent EP 0 564 476 or in International Patent Application WO 94/23005 - be adsorbed on carrier substances and/or embedded in coating substances in order to protect them against premature inactivation. In the detergents of the invention they are present preferably in amounts of up to 5% by weight, in particular from 0.2% by weight to 4% by weight. Where the composition of the invention comprises protease, it preferably has a proteolytic activity in the range from about 100 PU/g to about 10,000 PU/g, in particular from 300 PU/g to 8000 PU/g. Where two or more enzymes are to be used in the composition of the invention, this may be accomplished by incorporating the two or more separate, or conventionally separately compounded, enzymes, or by means of two or more enzymes compounded together in granules, as known, for example, from International Patent Applications WO 96/00772 or WO 96/00773.

The organic solvents which may be used besides water in the compositions of the invention, especially if they are present in liquid or paste form, include alcohols having 1 to 4 carbon atoms, especially methanol, ethanol, isopropanol and tert-butanol, diols having 2 to 4 carbon atoms, especially ethylene glycol and propylene glycol, and also mixtures thereof and the ethers derivable from the aforementioned classes of compound. Water miscible solvents of this kind are present in the compositions of the invention preferably in amounts of not more than 30% by weight, in particular from 6% by weight to 20% by weight.

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In order to adjust the pH to a desired level which does not come about of itself through the mixing of the other components, the compositions of the invention may comprise system-compatible and environmentally 2.5 compatible acids, especially citric acid, acetic acid, tartaric acid, malic acid, lactic acid, glycolic acid, succinic acid, glutaric acid and/or adipic acid, or else mineral acids, especially sulfuric acid, or bases, especially ammonium hydroxides or alkali hydroxides. pH regulators of this kind are present in the compositions of the invention in amounts of preferably not more than 20% by weight, in particular from 1.2% by weight to 17% by weight.

35 Graying inhibitors have the function of keeping the soil detached from the textile fiber in suspension in the liquor. Suitable for this purpose are water soluble colloids, usually organic in nature, examples being starch, dlue, gelatin, salts of ether carboxylic acids or ether sulfonic acids of starch or of cellulose, or salts of acidic sulfuric esters of cellulose or of starch. Water soluble polyamides containing acidic groups are also suitable for this purpose. Furthermore, 5 starch derivatives other than those mentioned above may be used, aldehyde starches, for example. Preference is given to cellulose ethers, such as carboxymethylcelulose (Na salt), methylcellulose, hydroxyalkylcelulose and mixed ethers, such as methylhydroxyethylcelulose, methylhydroxypropylcelulose, methylcarboxymethylcelulose, and mixtures thereof, in amounts, for example, of from 0.1 to 5% by weight, based on the compositions.

15 As optical brighteners, laundry detergents of the invention may comprise derivatives of diaminostilbenedisulfonic acid and/or its alkali metal Suitable, for example, are salts of 4,4'-bis(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino) stilbene-2,2'-disulfonic acid or compounds of similar structure which 20 instead of the morpholino group carry a diethanolamino group, a methylamino group, an anilino group, or a 2-methoxyethylamino group. It is also possible for brighteners of the substituted diphenylstyryl type to 2.5 be present, for example, the alkali metal salts of 4,4'-bis(2-sulfostyryl)biphenyl, 4,4'-bis(4-chloro-3sulfostyryl)biphenyl, 4-(4-chlorostvrvl)-4'-(2or sulfostyryl)biphenyl. Mixtures of the aforementioned optical brighteners may also be used.

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Especially for use in machine processes, it may be of advantage to add customary foam inhibitors to the compositions. Examples of suitable foam inhibitors are soaps of natural or synthetic origin having a high  $C_{18}$ - $C_{24}$  fatty acid fraction. Examples of suitable nonsurfactant-type foam inhibitors are organopolysiloxanes and their mixtures with microfine, optionally silanized silica and also paraffins, waxes, microcrystalline waxes, and mixtures thereof with

silanized silica or bis-fatty acid alkylene diamides. With advantages, use is also made of mixtures of different foam inhibitors, for example, mixtures comprising silicones, paraffins, or waxes. The foam inhibitors, especially those containing silicone and/or paraffin, are preferably bound on a granular, water soluble or dispersible support substance. Particular preference is given to mixtures of paraffins and bisstearylethylenediamide.

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The production of solid compositions of the invention presents no difficulties and may be done conventionally, for example, by spray drying or granulation, with the enzymes and any other heat sensitive ingredients such as bleaches, for example, being added separately later on if desired. To produce compositions of the invention of heightened bulk density, in particular in the range from 650 g/l to 950 g/l, preference is given to a process known from European Patent EP 0 486 592 which includes an extrusion step. Another preferred preparation, with the aid of a granulation process, is described in European Patent EP 0 642 576

25 To produce compositions of the invention in tablet form, which may have one or more phases, may have one or more colors, and consist in particular of one layer or of two or more layers, in particular of two layers, it is preferred to follow a procedure in which all of the constituents - per one layer if appropriate - are mixed with one another in a mixer and the mixture is compressed by means of conventional tableting presses, for example, eccentric presses or rotary presses, at pressing forces in the range from about 50 to 100 kN, preferably from 60 to 70 kN. Especially in the case of multilayer tablets it may be of advantage if at least one layer is compressed beforehand. This is preferably accomplished at pressing forces of between 5 and 20 kN, in particular from 10 to 15 kN. In this way, tablets

which are fracture resistant and vet dissolve sufficiently quickly under application conditions are obtained without problems, having fracture strengths and flexural strengths of normally from 100 to 200 N, but preferably above 150 N. A tablet produced in this way preferably has a weight of from 10 g to 50 g, in particular from 15 g to 40 g. The three-dimensional form of the tablets is arbitrary and may be circular, oval or angular, with intermediate forms also being possible. Corners and edges are advantageously rounded. Circular tablets preferably have a diameter of from 30 mm to 40 mm. In particular, the size of tablets of angular or cuboid design which are introduced predominantly by way of the dosing apparatus of, for 15 example, the dishwashing machine is dependent on the geometry and on the volume of this dosing apparatus. Embodiments which are preferred by way of example have a basal area of (from 20 to 30 mm) × (from 34 to 40 mm), in particular of 2636 mm or of 24×38 mm. 20

Liquid or paste detergents of the invention in the form of solutions comprising customary solvents are generally prepared by simply mixing the ingredients, which may be introduced in bulk or in solution into an 25 automatic mixer.

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## What is claimed is:

- An amylase containing detergent, characterized in that it comprises  $\alpha$ -amylase from amyloliquefaciens and color transfer inhibitor, as well as customary ingredients compatible with such constituents.
- 2. The composition as claimed in claim 1, charac-10 terized in that it contains amvlase in amounts of from 0.001 mg to 0.5 mg, in particular from 0.02 mg to 0.3 mg, per gram of the overall composition.
- 15 3. The composition as claimed in claim 1 or 2, characterized in that it contains from 0.1% by weight to 2% by weight, in particular from 0.2% by weight to 1% by weight, of color transfer inhibitor.
  - The composition as claimed in any of claims 1 to 4. 3. characterized in that the color transfer inhibitor is a polymer of vinylpyrrolidone, vinvlimidazole, vinvlpvridine N-oxide, or a

copolymer of these.

- The composition as claimed in any of claims 1 to 5. 4. characterized in that the color transfer inhibitor is a polyvinylpyrrolidone having an 30 average molar mass in the range from 10,000 to 60,000, in particular from 25,000 to 50,000.
- The composition as claimed in any of claims 1 to 6. 4, characterized in that the color transfer 35 inhibitor is a copolymer of vinylpyrrolidone and vinylimidazole in a molar ratio of 5:1 to 1:1 having an average molar mass in the range from 5000 to 50,000, in particular from 10,000 to 20,000.

7. The composition as claimed in any of claims 1 to 3, characterized in that the color transfer inhibitor is a system comprising a peroxidase and hydrogen peroxide and/or a substance which in water provides hydrogen peroxide.

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- The composition as claimed in claim 7, characterized in that the system further comprises a
  mediator compound for the peroxidase.
- 9. The composition as claimed in claim 7 or 8, characterized in that the system further comprises a polymer of vinylpyrrolidone, vinylimidazole, vinylpyridine N-oxide or a copolymer of these.
- 10. The use of a combination of  $\alpha$ -amylase from Bacillus amyloliquefaciens and color transfer inhibitor for enhancing the cleaning performance of detergents with respect to starchy stains when used in washing and cleaning solutions, especially aqueous washing and cleaning solutions.
- 11. The use of a combination of α-amylase from 25 Bacillus amyloliquefaciens and color transfer inhibitor for preventing the transfer of textile dyes from dyed textiles to undyed or different-colored textiles when said textiles are laundered together in aqueous solutions, especially aqueous 30 solutions comprising surfactant.